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**AUTHOR(S):** N. E. Vanderborgh, J. P. Bertino, G. E. Cort, and P. Wagner

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los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545



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# HEAT TRANSFER THROUGH COALS AND OTHER NATURALLY OCCURRING CARBONACEOUS ROCKS*

N.E. Vanderborgh, J.P. Bertino, G.E. Cort and P. Wagner

Los Alamos Scientific Laboratory
P. O. Box 1663, MS-734
Los Alamos, New Mexico 87545 USA

## ABSTRACT

The understanding of heat transfer through solid fossil fuels is essential to the phenomonology of pyrolysis, gasification and combustion of these fuels. While coals have thermal conductivities of 0.1-0.5 W/mK at 300 K, heat transfer measurements are complicated by the changes found in these fuels caused by the heating processes. Such complications are clearly shown when one looks at thermal conductivity differences between virgin and heat-treated materials.

Coals, upon heating, undergo a variety of chemical and physical modifications. Initially, these materials lose low molecular weight gases; additional heating removes moisture. Such pyrolytic processes result not only in a significant mass decrease (as much as 50% for low-rank coals), but a marked alteration in the internal structure of the material. In virgin coals, mass transfer is dominated by a system of pores. Drying these materials typically alters the flow mechanisms and consequently the permeability. Heat transfer becomes dominated by the convective transport of products generated within the specimen during the heating process.

Studies are described that explore the concurrent and counter-current heat and mass transfer problems through semiporous materials such as coals and other model specimens.

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## INTRODUCTION

Even though vast quantities of subbituminous coals are known to exist under the semiarid regions of the Southwestern United States, the expanded development of this resource presents unusual problems. These coals show enough seam dip so that surface mining is rather limited; conservative estimates[1] suggest that less than 5% of the known reserve is within surface mining range. Moreover past experience with underground mining suggests that unusual technical problems result from the limited $H_2O$ supply, generally friable roofs, and the lenticular nature of these deposits. Thus the coal supply may permit only a modest expansion of current production rates, unless new extraction technologies are developed.

The Los Alamos Scientific Laboratory is exploring an approach that appears to have promise in expanding coal production in the Southwestern U.S. This approach involves an initial in situ preconditioning of coal. During this step the coal is chemically modified to offer low resistance (flow enhancement), and suitable chemistry underground. This thermal processing simultaneously yields a stream of hydrogen-enriched products and leaves a porous semichar that is used for underground gasification. This is shown schematically in Figure 1.

"Chemically mining" coal for underground conversion of this fossil resource to gaseous or liquid fuels, is not a new idea.[2] The concept of utilizing coal without the coincident societal and environmental costs of conventional mining has intrigued mankind for decades. Early experiments, mainly in Europe,[3-6] have identified the severe technical problems of developing and maintaining flow and reactivity conditions that may be dominated by the frequently unfavorable naturally occurring coal-seam properties. Initial successes resulted from the realization[7] that flow modification (reverse combustion) is necessary not only to change overall flow resistance but also to achieve a single controlled flow path of high permeability. The two-stage process described in this paper attempts to achieve the same type of control by first drying specific regimes in the coal and then effecting pyrolysis in those dried regions to release gaseous and liquid hydrocarbons. Once that process has occurred, then the highly porous seam will be subject to a variety of different processing options. This process concept has been developed for dry, Southwestern coals.

## DRYING AND PYROLYSIS OF SUBBITUMINOUS COALS

The structure of naturally occurring coals is complicated by the highly anisotropic nature of these materials. Here we assume we are dealing with "average coal". The flow behavior through

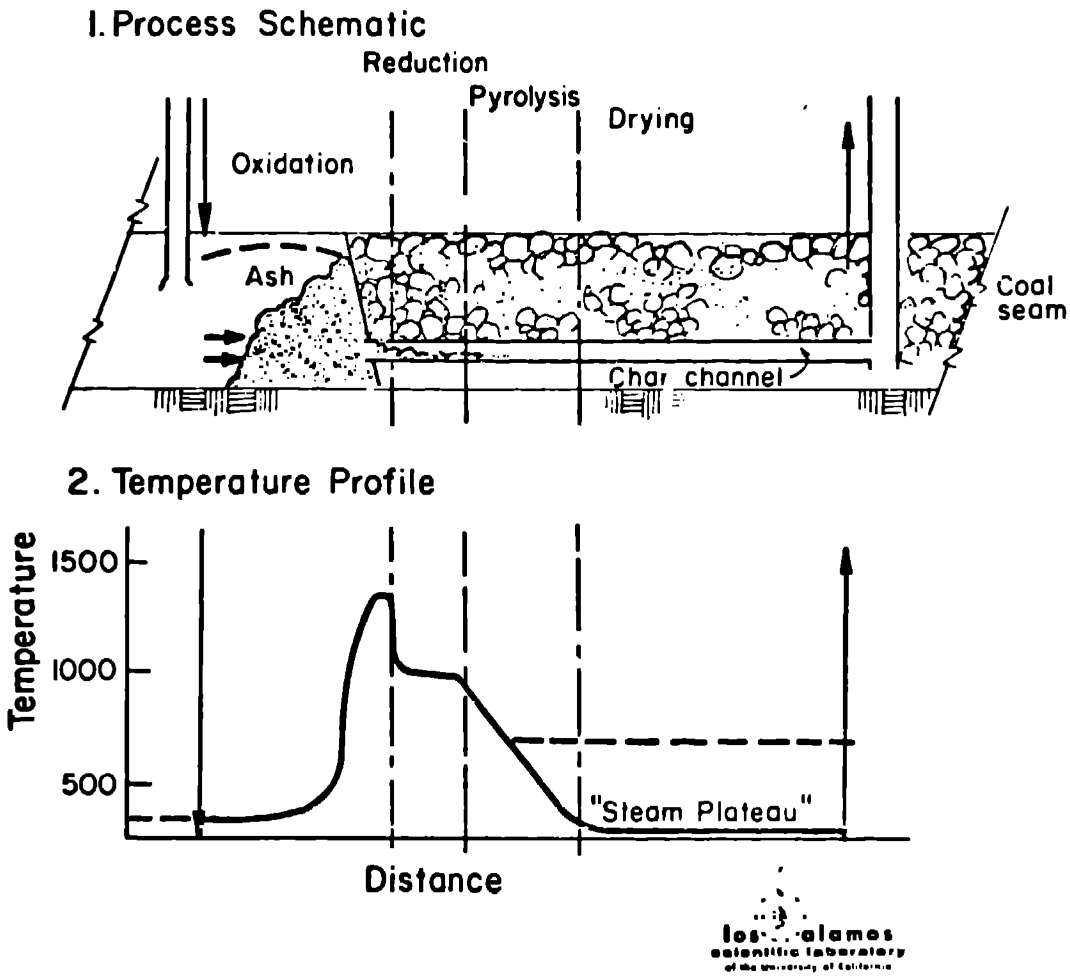


Figure 1. Underground Gasification of Southwestern U.S. Coal.

coals is explained by assuming that coal is a hardened gel, with various-sized, interconnecting pores and capillaries. Such connecting paths are typically emphasized in one direction. The majority of these pores, in virgin coal, are less than 50 nm. Due to these pores, coals exhibit a molecular sieve property excluding certain molecules while entrapping others. This sort of molecular discrimination results from chemical properties as well as from molecular size.

Moisture plays an essential role in initial flow distinctions. Water is typically absorbed in coal micropores. Moreover, water is a pore-filling material due to the fact that tetragonal bonding between a chemisorbed water molecule and an additional water molecule

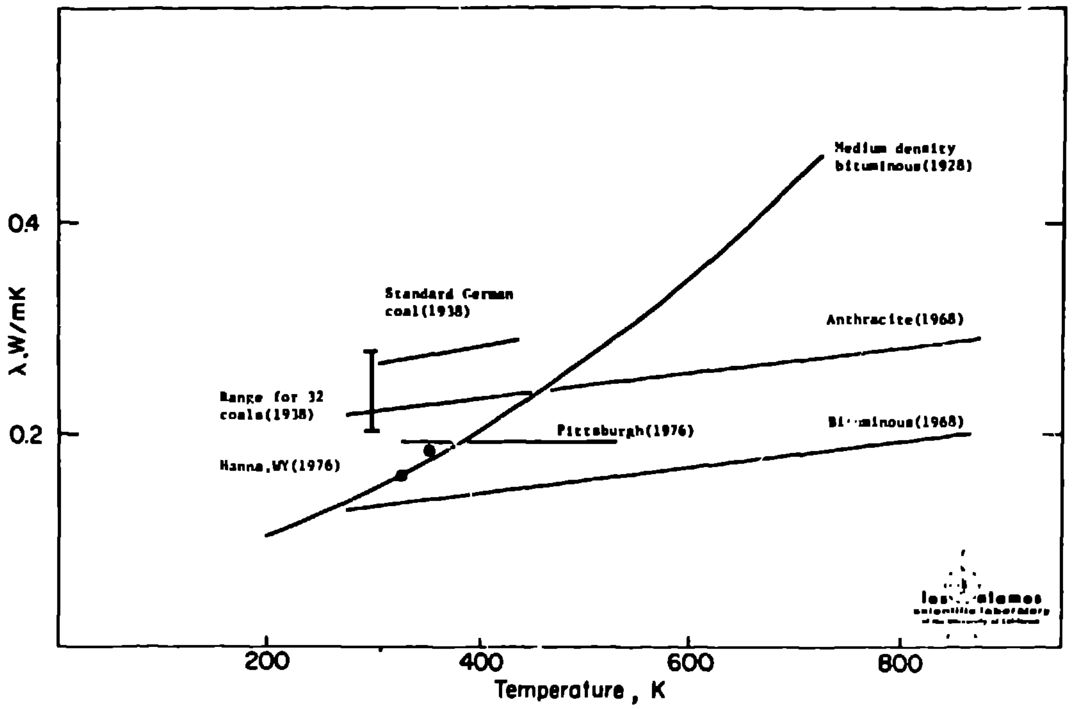


Figure 2. Thermal Conductivities of Coals.

is possible. Thus, the first significant flow enhancement process is pore-dewatering of these coals. This type of pore drainage is thought to be the first step in any drying process; pore dewatering apparently is the first essential mechanism in the promotion of methane drainage from coals.

Heating the coal is one possible approach to accomplish pore dewatering. Drying subbituminous coals leads to the formation of shrinkage cracks. Thus the removal of moisture changes the flow regime from one dominated by pores to that of one dominated by cracks. This process is known to lead to an increase in flow permeability, the volume of the gas moving in unit time through a fixed volume of coal caused by a pressure gradient, of approximately two to three orders of magnitude. It is obviously essential that the dewatering (drying) and subsequent shrinkage of these candidate coals be understood if one is to learn how to optimize the underground processes.

## HEAT TRANSFER THROUGH COALS

Figure 2 is a compilation of reported values[8-12] of thermal conductivities (λ) of various coals. It is clear from the figure that the differences in the reported values for $\lambda$ of virgin (i.e., unheated) coals are not large and appear to be independent of origin and rank. Not included in the figure are the room temperature data that we obtained on the coal samples from the open pit mine at Farmington, NM; however, these too fall in the 0.2 W $m^{-1}K^{-1}$ vicinity that seems to be characteristic for $\lambda$ of coal at about 300 K. It is seen from the figure that there is no simple relationship between temperature and $\lambda$.

The behavior of the thermal conductivities of coals with temperature gives us a clue to the mechanism of heat transport within coal. The thermal conductivity of a solid (neglecting higher order terms) is

$$\lambda = \lambda_{el} + \lambda_{l},$$

where $\lambda_{el}$ is the electronic transport term and $\lambda_l$ is the lattice component. The electronic term is evaluated from the Weidemann-Franz law by

$$\lambda_{el} = L \sigma T.$$

L is a constant and $\sigma$ is the electrical conductivity. For coals, $\sigma$ is very low and $\lambda_{el}$ is $<< \lambda_l$ so $\lambda \sim \lambda_l$. Peierls[13] showed, in 1929, that $\lambda_l$ goes as 1/T above the Debye temperature, $\theta_D$. Since there are probably a family of Debye temperatures for coal, let us consider coal by analogy with graphite which has an effective Debye temperature just above room temperature (this is stated this way because $\theta_D$ is different for the a-b plane and for the c-axis direction). Thus above 300 K the observed thermal conductivity for coal should drop with increasing temperature. But it doesn't, it goes up instead. One is forced to the conclusion that the classical rate determining mechanisms for thermal conductivity are not valid for coal- or perhaps we should start thinking in terms of coal systems. One mechanism that is consistent with the experimental observations is that of convection within the pores and cracks of the coal itself. It is postulated that in addition to the gases normally present in the coal pores, volatilization of the organic components of the coal provides a continuing source of gaseous matter with increasing temperature thus generating a system in which the flow of mass was really caused by the flow of heat and vice versa. Therefore it would be expected that steady state measurements of $\lambda$ for coal done as a function of temperature would reflect an ever increasing convective heat transfer contribution which would show up as an increase of $\lambda$ with increasing T -- which is what we see in Figure 2. Modelling of the coal gasification in terms of combined heat and mass transfer is consistent with the described heat transfer mechanism.

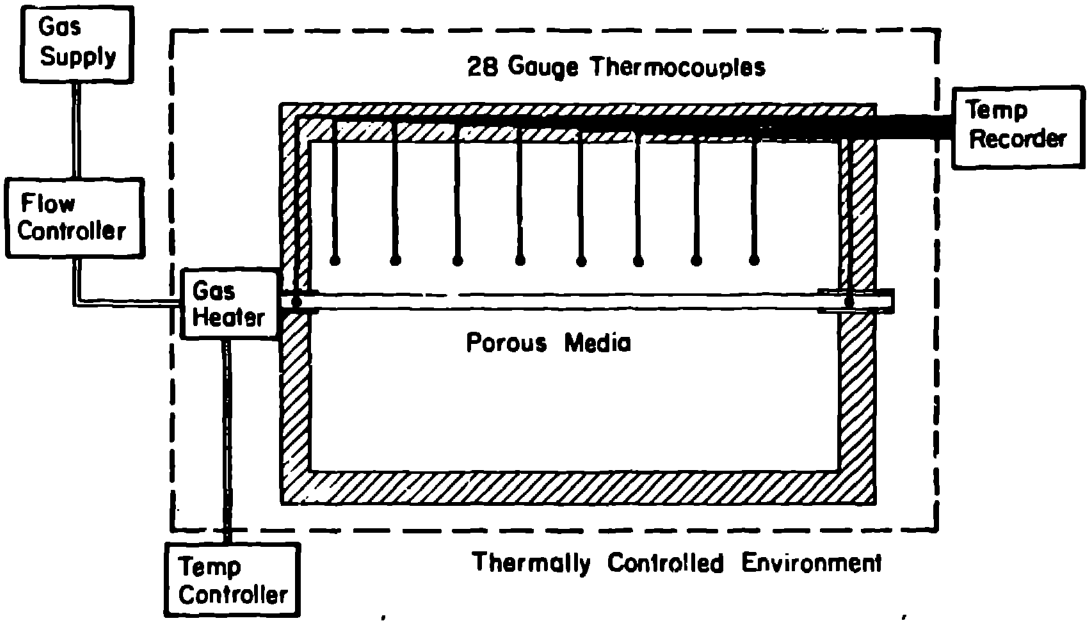


Figure 3. Schematic of Apparatus for Combined Heat and Mass Transfer Experiments.

## EXPERIMENTAL

The experimental and calculational tasks are to describe the states of flow that occur through media as the media are altered by the drying processes. Although several geometries may be possible, we chose to work with heating through a narrow channel bored within the center of a candidate sample. Figure 3 is a schematic of the experimental arrangement. The entire sample is bounded by a high-flow-resistance material so that the only mass transfer into the specimen is through the axial channel and the only transfer path out is also through the exit of that channel. This would be somewhat analogous to a low flow-resistance link, (for example, an explosively driven penetrator channel) connecting two vertical bores in a coal seam. It represents the type of geometry that might be best for the two-stage process.

Two different media were selected for study. The ideal material for such testing of the flow codes would have a highly homogeneous and well characterized permeability and porosity. Moreover, it should exhibit known moisture content and moisture transfer rates as well as heat transfer rates. It was decided that these properties would be best approached by using well known ceramic materials which could be cast in place around a central rod and around a series of temperature and pressure transducers. The rod would be removed to form the central channel. The relative dimensions and thermocouple positions of the first ceramic test section are shown in Figure 3. This specimen used highly porous gypsum, $CaSO_4 \cdot 2H_2O$, as the ceramic.

Experiments consisted of passing gases into the block at fixed inlet temperatures and at known flow rates. In this way, a known and controlled heat flux was introduced into the specimen and then, using thermocouples, the time dependent spatial distribution of that thermal energy was determined. Simultaneous heat and mass transfer with convective terms that caused the predominate effects were determined in this manner.

Other blocks of similar dimensions made from Southwestern subbituminous coals were prepared. In these cases, the central channel, with length/diameter ratio of 50, was bored through the specimen. Thermocouples were inserted into holes bored through the outer epoxy insulating sheath and then into the coal for a predetermined distance. After the thermocouples were inserted, holes were filled and sealed with additional epoxy. Both types of experiments were photographed using X-ray techniques to ascertain the exact positions of various transducers and flow channels.

## MODELLING THE COMBINED HEAT AND MASS TRANSFER

The calculations to describe heat transfer in these porous media were bounded by these particular flow geometries. These calculations were performed using a generalized finite-element heat conduction program, PANCHO. This code, which has been described by Vanderborgh et al,[14] describes the simultaneous flow and heat transfer in semiporous materials. The analytical approach specifies an estimated axial pressure distribution along a flow channel wall; this distribution is used as a boundry condition for the Darcy porous flow calculation. Conservation of mass is then invoked to adjust the flow in the central channel and the resulting wall pressure. The new wall pressure is used in succeeding iterations until the net flow in and out of the porous wall is zero, and the axial pressure distribution is converged. The flow solution is then included in the convective heat transfer terms, $C_p(V_r dT/dr + V_z dT/dz)$, which are used in the finite element heat conduction solution.

The model is also capable of extension to the following cases:

- inclusion of non-isotropic and spatially varying properties.
- inclusion of terms due to heat sources and sinks due to condensing and vaporizing fluids, including steam.
- inclusion of terms that compensate for mass sources and sinks due to the above.
- inclusion of fixed external pressure and temperature boundary conditions instead of sealed, insulated surfaces.
- inclusion of temporal variation of properties caused by changes in flow resistivities.

## RESULTS

Some of the early results from our combined heat and mass transfer experiments are shown in Figures 4 and 5. Figure 4 shows the thermal profiles measured in the gypsum block and compares those values to results predicted using the combined heat and mass transfer code, PANCHO. The mass transfer boundary, epoxy, and ceramic interface are shown. As indicated, the temperatures peak at this interface even though the thermal conductivity of the epoxy is considerably higher than that for the ceramic test specimen (0.48 W/m-K). These results show the final, steady state behavior of this system. Currently the code also depicts the dynamic thermal changes and can be used to study semiporous systems that have different mass transfer resistances during the course of the system.

Studies were also done to study the effects of drying ceramic blocks. Although it would have been feasible to introduce a fixed amount of water initially into the ceramic system, the difficulties of accomplishing this without adversely influencing the physical properties of the ceramic are apparent. Then, too, one would have to model the effects of a two-phase flow (gas and liquid), greatly increasing the complexity of the analytical model. Consequently the inverse experiment, that of wetting, was done. In this case liquid water was pumped at known, low rates (5 ml/min) through the inlet heater (400 K) and into the block which was maintained at a sufficiently high temperature that steam condensation should predominate. Results of this experiment were well predicted by the PANCHO code. First heating effects were concentrated at the inlet side of the block, this resulted in not only heat deposition but also partial blockage of the mass transfer channels. As a direct consequence, the steady state experiment showed that the exhaust side of the specimen saw the highest temperature.

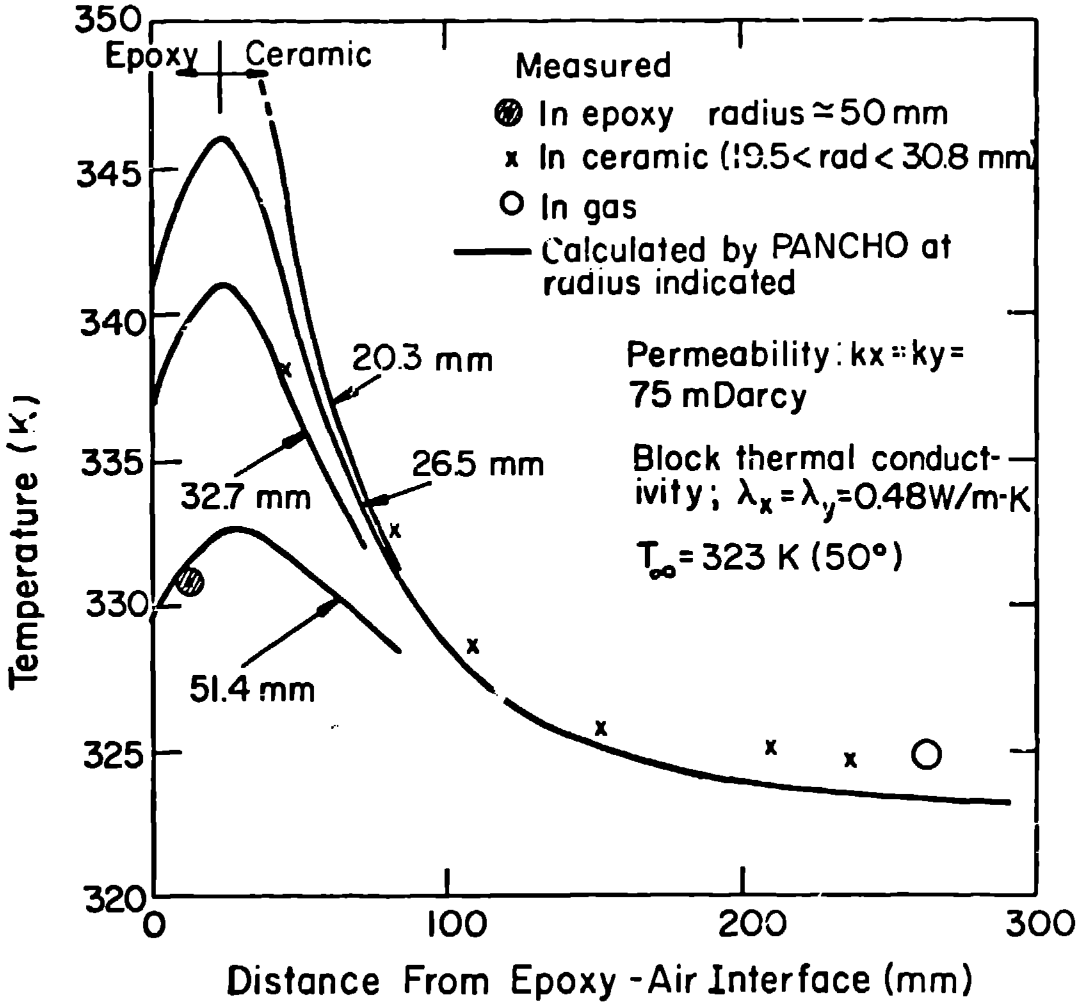


Figure 4. Temperature Profiles in $CaSO_4 \cdot 2H_2O$ Experiment.

Results on coal specimens are shown in Figure 5. These studies show that initially the heating removes moisture to cause a permeability increase in the inlet region. Indications are that the permeability increases from the initial approximately 0.1 md (millidarcies) to approximately 10 md. This permeability variation changes the heat transfer mechanism from one dominated by thermal conductivity variations to one dominated by mass transfer.

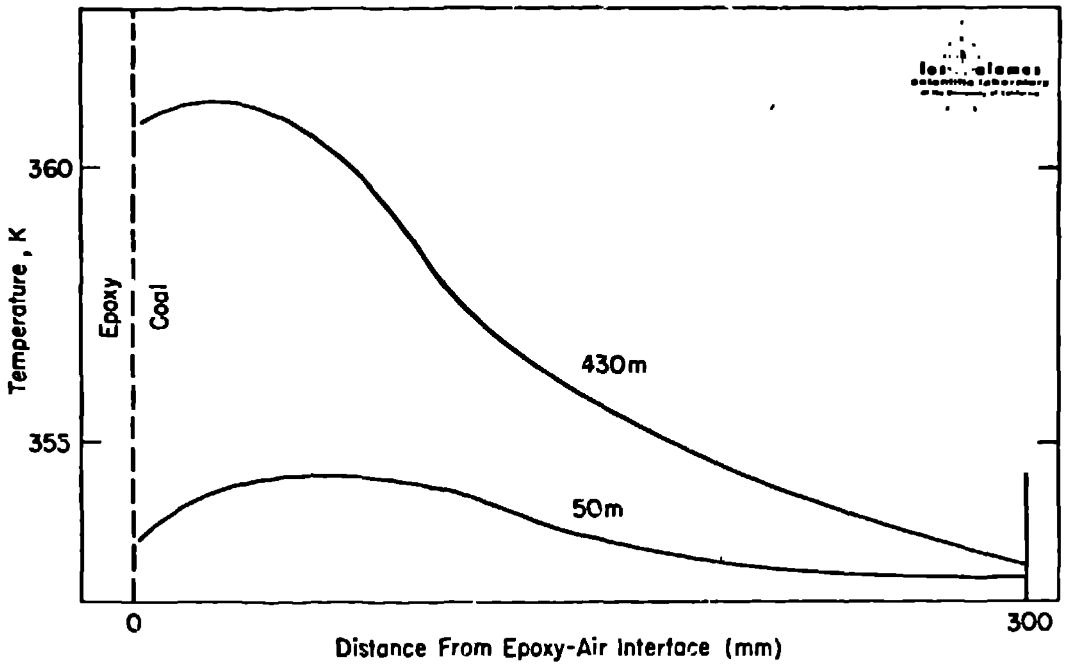


Figure 5. Temperature Profiles in San Juan Coal Hot-Gas Drying Experiment.

## SUMMARY

The temperature-time histories show clearly that heat transfer in these porous materials results almost entirely from convective heat transfer. The range of permeability studied here, near 3.5 mD, is what we expect to find in the middle of the drying-pyrolysis processing of thes Southwestern coals. These data strongly suggest that once this pyrolysis process begins, convective heat transfer can be efficiently used through out the resulting semi-porous media.

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